

at least in duplicate, with a Beckman Model G and a Metrohm Model E 300 pH meter, using glass-calomel electrodes. The instruments were checked with buffers at pH 4.00 and 9.00 and with pure benzoic acid before and after each series of runs; the values given in Table I should be correct within ± 0.05 pK units.

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The Reaction of Grignard Reagents with *N,N*-Dialkyl-*N*-(phenylthiomethyl)amines

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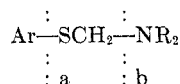
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Treatment of $\text{ArSCH}_2\text{NR}_2$ with $\text{R}'\text{MgX}$ generally produces $\text{R}'\text{CH}_2\text{NR}_2$ in good yields. The following amines were thus prepared: *N-n*-amyl-, *N*-isobutyl-, *N*-(*p*-dimethylamino)benzyl-, and *N*-(2,4,6-trimethyl)benzylpiperidine, as well as *N*-4-butenyl-, *N*-isobutyl-, and *N*-benzylmorpholine. The attempted preparation of *N*-neoamylpiperidine under similar conditions failed, *N*-methylpiperidine being formed.

The preparation of tertiary amines by treating *N*-alkoxymethyl-*N,N*-dialkylamines with Grignard reagents has been well established.^{3,4} There is also one report of the preparation of *N*-benzyl-*N,N*-dimethylamine from *N,N*-dimethyl-*N*-(nonylthiomethyl)amine.⁵

The analogous reaction with arylthiomethylamines has not been described. We were led to investigate this reaction as part of our studies of the cleavage patterns of arylthiomethylamines. *A priori*, two modes of cleavage are feasible, as shown. From

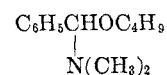


analogy to the alkoxymethylamines one would expect bond a to break and with a Grignard reagent $\text{R}'\text{MgX}$ to yield the tertiary amine $\text{R}'\text{CH}_2\text{NR}_2$. However, on the basis of a recent report concerning the mechanism of the acid-catalyzed rearrangement of *N*-arylthiomethyl-*N*-arylamines to *p*-arylthiomethylanilines,⁶ in which a cleavage to a resonance-stabilized sulfonium-carbonium ion is postulated, it was conceivable that bond b might break and yield with a Grignard reagent the corresponding sulfide $\text{ArSCH}_2\text{R}'$.

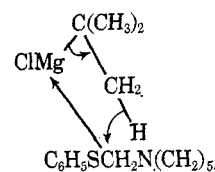
In all instances, with the exception of *t*-butylmagnesium chloride, the Grignard reagents, prepared in the usual fashion from the corresponding halides,⁷ yielded the expected tertiary amines in excellent yields. In Table I are listed the amines obtained from *N*-phenylthiomethylpiperidine, including boiling or melting points and the melting points of the picrates of these amines. In Table II are listed data concerning the amines obtained from *N*-phenylthiomethylmorpholine.

In general, the reactions carried out by adding an ether solution of the phenylthiomethylamine to the preformed Grignard reagent were very vigorous and rapid. In fact they had to be moderated by adding the

thiomethylamine slowly. The *t*-butylmagnesium chloride and the 2,4,6-trimethylphenylmagnesium bromide were exceptions. The former had to be refluxed for a long time and the expected neoamylpiperidine did not form to any significant extent, if at all. Instead a reduction to *N*-methylpiperidine took place with a simultaneous liberation of isobutylene. This is undoubtedly due to steric hindrance to which Grignard reactions are sensitive. It is analogous to the reduction of α -methyl- α -piperidineacetonitrile to *N*-ethylpiperidine⁸ and of α -dimethylaminobenzyl butyl ether



to *N,N*-dimethylbenzylamine⁹ by *t*-butylmagnesium bromide. The following six-membered cyclic transition state is most likely involved.



It is remarkable that, though reacting sluggishly, the mesitylene derivative forms the corresponding amine in a yield of 81% of the theory, when the reaction is carried out at the temperature of refluxing tetrahydrofuran. Since the methyl groups are in the plane of the benzene ring, there is little steric resistance to the attack of the Grignard reagent from a side perpendicular to the plane of the ring.

When employing bromobenzene, it was found that it is not necessary to preform the Grignard reagent, but rather the reaction, once started, proceeds very vigorously with equally good yields when all of the reactants are introduced together, *i.e.*, when $\text{C}_6\text{H}_5\text{Br}$ and $\text{C}_6\text{H}_5\text{SCH}_2\text{NR}_2$ in ether are added to a suspension of magnesium turnings in ether. This appeared surprising for sulfide compounds have been reported as inhibiting the formation of the Grignard reagent.¹⁰ When

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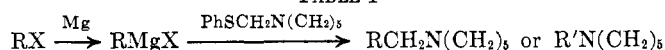
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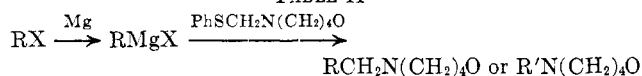
TABLE I



RX	R'	Bp (mm), °C	Mp, °C	Yield, %	Mp of picrate, °C
<i>n</i> -C ₄ H ₉ Br	<i>n</i> -C ₅ H ₁₁	196–197 ^a (760)		86	104–106 ^b
<i>i</i> -C ₃ H ₇ Br	<i>i</i> -C ₄ H ₉	160–162 ^c (760)		71	142–144 ^d
C ₆ H ₅ Br	C ₆ H ₅ CH ₂	120–121 ^e (13)		82	178–180 ^f
<i>p</i> -(Me ₂ N)C ₆ H ₄ Br	<i>p</i> -(Me ₂ N)C ₆ H ₄ CH ₂	158–164 ^g (4–5)	40–42	78	158–160
2,4,6-Me ₃ C ₆ H ₂ Br	2,4,6-Me ₃ C ₆ H ₂ CH ₂	109–110 (2)		81	198–200

^a Lit.³ bp 196° (760 mm). ^b Lit.³ mp 107°. ^c T. J. King [*J. Chem. Soc.*, 898 (1951)] reports bp 161–163° (760 mm). ^d T. J. King (footnote c) reports mp 144–145°. ^e T. J. King (footnote c) reports bp 115° (13 mm). ^f T. J. King (footnote c) reports mp 178–179°. ^g H. F. Tseou and Y. T. Wang [*J. Chinese Chem. Soc.*, 4, 418 (1936); *Chem. Abstr.*, 31, 1811 (1937)] report mp 43°.

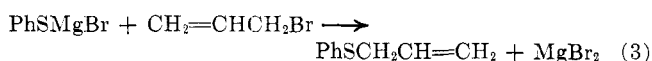
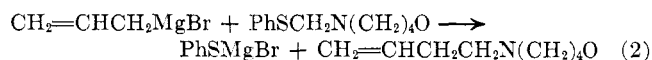
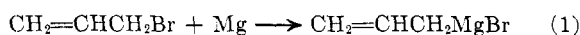
TABLE II



RX	R'	Bp (mm), °C	Yield, %	Mp of picrate, °C
CH ₂ =CHCH ₂ Br	CH ₂ =CH-CH ₂ CH ₂	180–187 (760)	75	115.5–116.5
<i>i</i> -C ₃ H ₇ Br	<i>i</i> -C ₄ H ₉	167 ^a (760)	68	129–131 ^b
C ₆ H ₅ Br	C ₆ H ₅ CH ₂	253 ^c (760)	85	188–190 ^d (2)

^a G. Opitz and A. Griesinger [*Ann.*, 665, 101 (1963)] report bp 65.5° (19 mm). ^b G. Opitz and A. Griesinger (footnote a) report mp 139°. ^c L. P. A. Fery and L. van Hove [*Bull. Soc. Chim. Belges*, 69, 79 (1960); *Chem. Abstr.*, 55, 4476 (1961)] report bp 104° (4 mm). ^d L. P. A. Fery and L. van Hove (footnote c) report mp 186–187.9°. J. P. Mason and M. Zief [*J. Am. Chem. Soc.*, 62, 1450 (1940)] report mp 193.5–195°.

allyl bromide was run in a similar manner without performing the Grignard reagent, in addition to the expected 4-butenylamine, allyl phenyl sulfide was isolated in good yields. The reaction can be rationalized as shown in eq 1–3. This was substantiated by prepar-

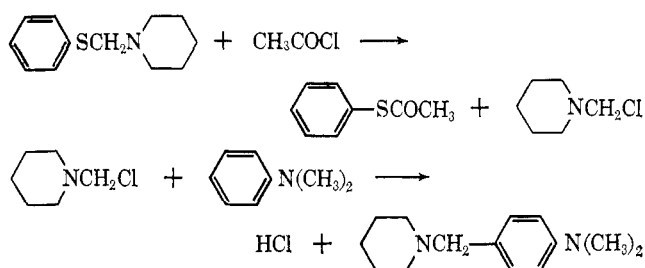


ing the allyl phenyl sulfide by treating allyl bromide with preformed phenylthiomagnesium bromide and thus we have rediscovered a method of preparing thioethers previously described by Taboury.¹¹

The preparation of tertiary amines by the method described in this paper offers advantages over the analogous preparations from the alkoxymethylamines. The phenylthiomethylamines are readily prepared in good yields¹² and once formed are stable, whereas the alkoxy compounds are reported to decompose even on standing.^{3,4} By a slight modification of the method described in the literature, the phenylthiomethylamines can be obtained in yields exceeding 95% of the theory. This Grignard method should be of particular advantage in the N-monoalkylation and N,N-dialkylation of aromatic amines, which we are currently investigating, as ArSCH₂NHAr' and (ArSCH₂)₂NAr' are known,¹³ while the corresponding oxygen analogs have not been reported.

N-(*p*-Dimethylaminobenzyl)piperidine was prepared by the action of *p*-dimethylaminophenylmagnesium

bromide on N-phenylthiomethylpiperidine, as well as by the action of acetyl chloride on the latter substance in the presence of dimethylaniline. The action of acetyl chloride on phenylthiomethylpiperidine can be rationalized by the equations shown.¹⁴



Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Infracord. The nmr spectra for all compounds prepared were obtained on a Varian A-60 nmr spectrometer and confirm the structures assigned to these. However, with the exception of N-phenylthiomethylmorpholine, the nmr spectra are not reported in this paper.

Materials.—Allyl, isopropyl, *n*-butyl bromide, and bromobenzene were obtained commercially and were used without further purification. *t*-Butyl chloride (bp 49.5°) was prepared from *t*-butyl alcohol and concentrated HCl.¹⁵ *p*-Bromo-N,N-dimethylaniline was prepared by bromination of N,N-dimethylaniline in glacial acetic acid,¹⁶ and melted at 53–55° upon recrystallization from alcohol. Bromomesitylene [bp 69–72° (2 mm)] was prepared by bromination of mesitylene.¹⁷

N-Phenylthiomethylpiperidine.—This compound was prepared by the following modification of the method of Grillo, *et al.*¹² In a 1-l., round-bottom flask, equipped with a stirrer, reflux condenser, addition funnel, and thermometer, was placed 230 g (2 moles) of practical grade thiophenol and 170.4 g (2 moles) of practical grade piperidine. Immediately an exothermic reaction commenced with the internal temperature rising to 65°. Without cooling, there was introduced into this reaction mixture 152 ml of formaldehyde (37%, 2 moles) over a period of 5 min. The reaction mixture was then refluxed for 30 min, whereupon it separated into two liquid phases. After cooling, the two phases were separated. The lower oily layer was then washed with 10% NaOH, extracted with ether, and dried with KOH pellets. After removal of the volatile solvent, the residue was separated by fractionation under reduced pressure. After a small forerun, there was collected 395 g (yield 95% of the theory) of a colorless liquid distilling at 138–141° (2 mm) [lit.¹² bp 138–141° (5 mm), yield 67% of theory]. Its infrared spectrum between salt discs agrees with Sadtler's spectrum (no. 3467) for N-phenylthiomethylpiperidine.¹⁸

(14) H. Böhme, E. Mundlos, W. Lehnert, and O. E. Herboth, *Ber.*, 90, 2008 (1957); H. Böhme and K. Hartke, *ibid.*, 93, 1305 (1960).

(15) S. V. Puntambeker and E. A. Zoellner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 524.

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(17) L. I. Smith, *Org. Syn.*, 11, 24 (1931).

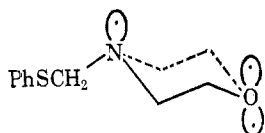
(18) "Sadtler Standard Spectra," Vol. 3, Midget ed, Samuel P. Sadtler and Son, Philadelphia, Pa., 1966.

(11) F. Taboury, *Bull. Soc. Chim. France*, [3] 29, 761 (1903); *Chem. Zentr.*, 2, 620 (1903).

(12) G. F. Grillo, *et al.*, *J. Am. Chem. Soc.*, 76, 3969 (1954).

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N-Phenylthiomethylmorpholine.—This compound was prepared in the same fashion as its piperidine analog which was described above. The resulting colorless oil was collected at 154–159° (2–3 mm) and was obtained in a yield of 94% of the theory [lit.¹² yield 33% of the theory, bp 146–149° (5–6 mm)]. Its nmr spectrum exhibited five types of protons: multiplets at 2.48 and 3.53, a singlet at 4.32, and two sets of aromatic multiplets centered at 7.25 and 7.47 ppm with area ratios of 4:4:2:3:2, respectively. The multiplets at 2.48 ppm are assigned to the N(CH₂)₂ protons, while those at 3.53 are assigned to the CH₂-OCH₂ protons. These, however, were not simple triplets in a 1:2:1 ratio, as one would expect if these protons were equivalent. They have a pattern of five lines in approximately the ratio of 1:0.5:1:0.5:1, in which the first and fifth lines were separated from the center line by approximately 5 cps, while the second and fourth lines were separated from this center line by about 1 cps. This unusual pattern was observed with all morpholine compounds and suggests that even at room temperature these compounds have a frozen conformation in which the usual chair-chair interconversions of the cyclohexane structure are inhibited by the electrostatic repulsion of the unbounded electrons on the heteroatoms.¹⁹ The phenylthiomethyl group, being bulky, is undoubtedly in the equatorial position and the molecule, most likely, has the conformation²⁰ shown.



Reactions of Phenylthiomethylamines with Grignard Reagents.—The preparation of N-*n*-amylpiperidine is typical of most of these reactions and is, therefore, described in detail. In a 1-l., three-neck, flask equipped with an efficient condenser to which is attached a CaCl₂ drying tube, a stirrer, an additional funnel, and a thermometer, was placed 5.4 g (0.22 g-atom) of magnesium turnings. The magnesium was covered with 100 ml of dry ether, and 2 ml of *n*-butyl bromide and a crystal of iodine were added. Once the reaction started, an additional 21.0 ml (0.2 mole) of *n*-butyl bromide, diluted with 50 ml of ether, was added dropwise over a period of 1 hr. At the end of the addition, the reaction mixture was refluxed for an additional 30 min. There was then introduced a solution of 20.7 g (0.1 mole) of phenylthiomethylpiperidine in 100 ml of ether over a 5-min period. The reaction mixture was then refluxed for another hour, cooled in an ice bath, and transferred to a 2-l. separatory funnel containing about 500 g of ice. The white slurry that formed was broken up by the addition of approximately 20 g of ammonium chloride. The ether phase was separated and the aqueous phase was extracted with two 100-ml portions of ether. These ether extracts were combined and washed with 10% NaOH. The resulting aqueous phases from this washing were combined for subsequent recovery of thiophenol. The ether phase was made acid using 2 *N* HCl, was separated, and was washed twice with water, followed by drying with anhydrous magnesium sulfate. Neutral components were later separated from this phase. The resulting acidic, aqueous phase was made basic with 10% NaOH and was then extracted with three 50-ml portions of ether. The extracts were combined, dried over KOH pellets, and separated; the ether was removed; and the residue was fractionated using a short Vigreux column. There was obtained 14.3 g of a colorless liquid, bp 196–197°.

The aqueous phase was acidified and extracted with ether. After drying over anhydrous magnesium sulfate, the ether was removed and the residue was fractionated, giving a yield of 8 g of a colorless liquid distilling at 40–41° (2 mm). Its infrared spectrum and odor were identical with those of thiophenol. This amounted to a 73% recovery of the thiophenol employed in this reaction.

The neutral components, upon removal of solvent, amounted to about 1 g. The infrared spectrum of this neutral material exhibited all of the absorption bands of *n*-octane when compared with Sadtler's spectrum (no. 5245),¹⁷ but it also showed a mono-substituted benzene ring. On standing overnight, long needles

formed, which melted at 57–60° and which showed no mixture melting point depression when mixed with an authentic sample of diphenyl disulfide (lit.²¹ mp 61.5°).

N-*p*-(N',N'-Dimethylamino)benzylpiperidine.—Three grams of magnesium turnings was covered with 50 ml of THF and a crystal of iodine was added. To this was added dropwise a solution of 22 g (0.11 mole) of *p*-bromo-N,N-dimethylaniline in 50 ml of THF. After an induction period of about 30 min, the reaction started and the reaction mixture was refluxed for 1 hr. A solution of 20.7 g (0.10 mole) of phenylthiomethylpiperidine in 50 ml of ether was added and refluxing was continued for another 30 min. The subsequent procedure for isolation of product was identical with that described above for N-*n*-amylpiperidine. After removal of the ether-THF solvent two fractions were obtained. The first fraction, boiling at 79–85° (4–5 mm), amounted to 1.62 g and by its infrared spectrum was identified as N,N-dimethylaniline. The second fraction consisted of 17 g of a colorless oil distilling at 158–164° (4–5 mm). Upon cooling in Dry Ice, crystals melting at 36–39° were obtained, which upon recrystallization from alcohol melted at 40–42°. The infrared spectrum had a strong absorption band at 12.3 μ, and an absorption pattern between 5 and 6 μ that confirms that this compound is a *para*-disubstituted benzene.

The picrate, which was deep orange in color was recrystallized from alcohol and melted at 158–160°.

Anal. Calcd for C₂₀H₂₆N₂O₇: C, 53.68; H, 5.64; N, 15.62. Found: C, 53.69; H, 5.84; N, 15.32.

The Dichlorochloride of N-*p*-(N',N'-Dimethylamino)benzylpiperidine.—In a three-neck flask was placed 12 ml (0.1 mole) of N,N-dimethylaniline, 100 ml of benzene, and 20.7 g (0.1 mole) of phenylthiomethylpiperidine. The solution was cooled in an ice bath and to this was added 7.5 ml of acetyl chloride in 50 ml of benzene, which was added over a period of 5 min. At first a clear solution was obtained. However, on warming to room temperature a white precipitate formed. The reaction mixture was refluxed for 15 min, and upon cooling was filtered and the residue was washed with three 20-ml portions of benzene. After recrystallization from alcohol, crystals were obtained which melted at 214–216°. A few grams of these crystals were dissolved in water, made basic, and extracted with ether. After drying over KOH pellets and removal of the solvent, the residual oil had an infrared spectrum identical with that obtained for N-*p*-(N',N'-dimethylamino)benzylpiperidine which was obtained as described above. On chilling it crystallized and a mixture of the materials obtained from these different methods gave no melting point depression. The yield amounted to 26% of the theory.

Anal. Calcd for C₁₄H₂₄Cl₂N₂: Cl, 24.37. Found: Cl, 24.60.

N-(2,4,6-Trimethyl)benzylpiperidine.—To 3 g of magnesium turning covered with 50 ml of THF was added a crystal of iodine and 2 ml of bromomesitylene. The reaction mixture had to be heated for more than 1 hr to start the reaction. Then an additional 15 g (0.075 mole) of bromomesitylene was added over a 30-min period; the mixture was refluxed for 2 hr more. To this was added 10.4 g (0.05 mole) of phenylthiomethylpiperidine. No vigorous reaction ensued at this point. The reaction mixture was then refluxed for 16 hr and the products were isolated according to the procedure described for N-*n*-amylpiperidine above. After removal of the solvent, the amine was isolated as a colorless oil, bp 109–110° (2 mm). The yield was 8.72 g or 81% of the theory. The 0.62 g of the residue had the same infrared spectrum as the distillate, raising the yield to 86% of the theory.

Its picrate (mp 198–200°) was obtained as light yellow needles from alcohol.

Anal. Calcd for C₂₁H₂₆N₄O₇: C, 56.50; H, 5.65; N, 12.55. Found: C, 56.61; H, 5.81; N, 12.30.

Reaction of *t*-Butylmagnesium Chloride with Phenylthiomethylpiperidine.—From the reaction of *t*-butylmagnesium chloride, prepared from 14.4 g (0.6 g-atom) of magnesium turnings and 37 g (0.4 mole) of *t*-butyl chloride, with 41.4 g of phenylthiomethylpiperidine, there was isolated 14.7 g (75% of the theory) of N-methylpiperidine, boiling at 104–106°. Its reported boiling point is 107°. Its picrate melts at 223–225°.²³

Thiophenol, isobutylene, and a small amount of 2,2,3,3-tetramethylbutane and diphenyldisulfide, but no N-*neo*-amylpiperidine, were identified as the other products of this reaction.

(19) M. Aroney and R. J. W. LeFevre, *J. Chem. Soc.*, 3002 (1958).

(20) It has been called to our attention that, although a plausible explanation, this is not the only possible one. A study of the nmr spectrum at various temperatures would possibly affirm or deny this explanation.

(21) W. Steinkopf, I. Schubart, and S. Schmidt, *Ber.*, **61**, 680 (1928).

(22) A. W. Hofmann, *ibid.*, **14**, 666 (1881).

(23) R. Lukes [Collection Czech. Chem. Commun., **12**, 71 (1947); *Chem. Abstr.*, **41**, 4150a (1947)] reports a melting point of 223–224° for this picrate.

N-4-Butenylmorpholine.—From the reaction of 20.9 g (0.1 mole) of phenylthiomethylmorpholine and the Grignard reagent formed from 24 g (0.2 mole) of allyl bromide, there was obtained 10.6 g of this compound (75% of the theory) that distills at 180–181°. In addition to the C–O–C and C–N bands of morpholine, its infrared spectrum showed absorption bands at 2.32, 6.68, and 11.0 μ , characteristic of monosubstituted vinyl compounds. (See Table II.) The picrate (from alcohol) had mp 115.5–116.5°.

Anal. Calcd for C₁₄H₁₈N₄O₇: C, 45.40; H, 4.90; N, 15.13. Found: C, 45.67, 4.72; N, 15.55.

In another run a solution of 15.7 g (0.13 mole) of allyl bromide and 20 g (0.1 mole) of N-phenylthiomethylmorpholine in 50 ml of ether was added to a suspension of 2.4 g (0.1 g-atom) of magnesium turnings in 100 ml of ether, without performing the Grignard reagent. The amine was obtained in only a 35% yield and from the neutral fraction was isolated in 28% yield allyl phenyl sulfide based upon the use of 0.1 mole of the N-phenylthiomethylmorpholine. Its infrared spectrum was identical with that of a sample of allyl phenyl sulfide prepared by the action of allyl bromide on C₆H₅SMgBr (see below).

N-Isobutylmorpholine.—Reaction of the Grignard reagent prepared from 25 g (0.2 mole) of isopropyl bromide with 20 g (0.1 mole) of phenylthiomethylmorpholine produced 9.8 g (68% of theory) of a colorless oil that had bp 167°. (See Table II.) The picrate (from alcohol) had mp 129–131°.

Anal. Calcd for C₁₄H₂₀N₄O₈: C, 45.15; H, 5.41; N, 15.05. Found: C, 45.22; H, 5.49; N, 15.15.

N-Benzylmorpholine.—From the reaction of 20 g (0.1 mole) of phenylthiomethylmorpholine with the Grignard reagent obtained from 23.59 g (0.15 mole) of bromobenzene there was collected 14.8 g (85% of the theory) of a colorless oil boiling at 73° (2 mm) and 253° (760 mm). The infrared spectrum of this compound showed strong bands at 13.5 and 14.3 μ typical of monosubstituted benzene rings. (See Table II.)

Allyl Phenyl Sulfide.—A solution of phenylmagnesium bromide in 100 ml of ether was prepared from 32 g (0.2 mole) of bromobenzene and magnesium turnings. This was converted into C₆H₅SMgBr by adding 17.6 g (0.16 mole) of thiophenol and refluxing for a short time. To this reaction mixture was then added 18 g (0.15 mole) of allyl bromide followed by refluxing for 3 hr. After hydrolysis with dilute HCl, the organic phase was washed with 10% NaOH and dried with anhydrous MgSO₄, and the volatile solvent was removed. From the residue was obtained 16 g (or 71% of the theory based upon the use of 0.15 mole of allyl bromide) of the thio ether, bp 68–75° (5–6 mm) and 219° (760 mm).²⁴ Its infrared spectrum had the characteristic absorption bands of terminal vinyl groups which appear at 6.02 and at 10.8 μ .

(24) C. D. Hurd and H. Greengard [*J. Am. Chem. Soc.*, **52**, 3356 (1930)] report bp 104–106° (25 mm) and 215–218° (750 mm).

The Reactions of Allylamines with Dichlorocarbene¹

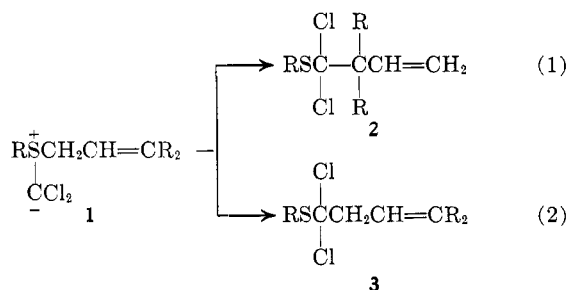
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The reaction of four allylamines, in which the basicity of the nitrogen is varied by appropriate substitution, with potassium *t*-butoxide–chloroform, *n*-butyllithium–carbon tetrachloride, and, in one case, ethyl trichloroacetate–sodium methoxide is reported. These amines, unlike the sulfur analogs, give cyclopropanes, and the yield of cyclopropane varies inversely with the basicity of the amine. In one case, an amide derived by a Stevens-type rearrangement was identified as a reaction product.

It has been shown that acyclic allyl sulfides react³ with ethyl trichloroacetate and sodium methoxide (dichlorocarbene) to give products derived by allylic



rearrangement of sulfur ylid 1 (eq 1), and, to a lesser extent, products derived by a Stevens-type rearrangement of 1 (eq 2). No cyclopropanes corresponding to addition of dichlorocarbene to the olefinic double bond have been observed in such reactions, an observation which suggests that the sulfur atom is more nucleophilic than the π -olefin bond to dichlorocarbene.

We wished to compare the course of reaction of acyclic allylamines with dichlorocarbene with the analogous reactions with allyl sulfides, and it was of particular interest to gain information relative to the effect of substitution on nitrogen on the reaction course.

(1) Supported by the U. S. Army Research Office (Durham) Contract No. DA-31-124-ARO-D-152.

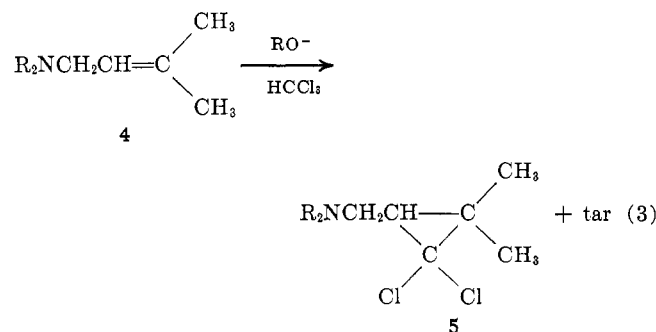
(2) From the Ph.D. Thesis of J. R. Potoski, the University of Minnesota, 1966.

(3) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **31**, 1694 (1966).

Procedure

A. Reactions with Potassium *t*-Butoxide–Chloroform.—Each of these reactions was effected using amine (1 equiv), chloroform (2 equiv), and potassium *t*-butoxide (2 equiv) in benzene at 0°. The reaction mixtures were processed by chromatography and/or distillation, and in some cases also by extraction with dilute hydrochloric acid to separate neutral components. Products were examined by thin layer chromatography and particular attention was given to the possible presence of trichlorovinylamines. The trichlorovinylamines are normal reaction products of allyl amines with phenyl(trichloromethyl)mercury.⁴ In no case were such products detected.

The course of reaction of the amines studied is shown in eq 3, and the results are summarized in Table I.



(4) W. E. Parham and J. R. Potoski, *ibid.*, **32**, 278 (1967).